Mechanism of Oxidation of p-Phenylene-diamine by Manganese(III) Acetate in Aqueous Sulphuric Acid Medium

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Oxidation of p-phenylenediamine by manganese(III) acetate in aqueous sulphuric acid medium is first order each in [Amine] and [Mn(III)]. Increase in [H^+] decreases the pseudo-first order rate constant and added Mn^{2+} has no effect on the rate. The reaction shows a positive salt effect. The reaction product has been isolated and characterised as p-benzoquinone. The probable mechanism involves formation of a complex between monoprotonated amine and Mn(III), which decomposes in a slow step to form the product.

It has been suggested that many manganese(III) complexes are likely to have biological relevance as model systems[1]. The manganese(III) porphyrin complexes have been studied[1,2] as possible models for the closely related and biologically important Fe system. A number of kinetic studies using manganese(III) perchlorate in perchloric acid, manganese(III) sulphate in sulphuric acid and manganese(III) acetate in acetic acid medium have been published and these were the subject of a review by Davies[3]. However, so far no attempt has been done using manganese(III) acetate in sulphuric acid medium. Manganese(III)-p-phenylenediamine system is a possible model for the oxidation of p-phenylenediamine by some bacteria/enzyme[4]. Therefore, it was thought of interest to study the kinetics of oxidation of p-phenylenediamine by manganese(III) acetate in sulphuric acid medium.

Solution of manganese(III) acetate was always prepared afresh in $10 N$ H_2SO_4 and estimated iodometrically. p-Phenylenediamine (Koch-Light) was recrystallised twice from ethanol. The ionic strength (μ) of the medium was maintained using sodium sulphate. All the other reagents used were of AR (BDH) grade. All solutions were prepared in doubly distilled conductivity water.

The requisite reaction mixture and required amount of p-phenylenediamine were separately equilibrated at the desired temperature and mixed. Aliquots (5 ml each) were withdrawn at regular time intervals and the unreacted Mn(III) estimated iodometrically. For all runs [Mn(III)]$_o$ was less than [p-phenylenediamine]$_o$, [H^+] and [Mn^{2+}]$_o$.

The stoichiometry of the reaction was determined by mixing Mn^{3+} and p-phenylenediamine in various proportions ([Mn^{3+}] always in excess over [p-phenylenediamine]) and estimating remaining unreacted Mn^{3+}. It was found that 2 mol of Mn(III) reacted with 1 mol of p-phenylenediamine to give 2 mol of Mn(II) and 1 mol of p-benzoquinone. The product, p-benzoquinone was isolated from the reaction mixture by extraction with ether and characterised by UV, IR and direct comparison with an authentic sample.

The kinetic results can be summarised as follows: (i) The disappearance of Mn(III) follows a perfect first order up to 40% of the reaction. The first order rate constants at various [Mn(III)]$_o$ and at constant [amine] remain almost unchanged. However, at varying [amine]$_o$ and constant [Mn(III)] the rate constants are directly proportional to [amine]$_o$ (Table 1). The plot of $1/k_{obs}$ versus $1/$[amine] at constant [H^+] is linear with a positive intercept indicating a possible complex formation between amine and Mn(III). (ii) The pseudo-first order rate constant decreases with increase in [H^+] (Table 2). At constant [amine] a plot of $1/k_{obs}$ versus [H^+] is linear with positive intercept showing a possible interaction between some reacting intermediate and the hydrogen ion. (iii) The reaction shows a positive salt effect. The observed rate constant does not change with change in [Mn^{2+}] (Table 2).

Under the reaction condition, reactive substrate species may be either the diprotonated amine or the

Table 1—Effect of Varying [Amine] and [Mn(III)] on the Pseudo-first Order Rate Constants

[Mn(II)] = 0.02 mol dm^{-3}; [H^+] = 1.0 mol dm^{-3}; μ = 2.00 mol dm^{-3}; temp. = 35°C

[Amine] (mol dm^{-3})	[Mn(III)] $\times 10^3$ (mol dm^{-3})	$k_{obs} \times 10^2$ (min^{-1})
0.0500	3.76	6.91
0.0625	3.76	9.90
0.0750	3.76	11.36
0.0875	3.76	12.66
0.1000	3.76	14.92
0.1250	3.76	17.96
0.0500	2.39	6.50
0.0500	4.78	6.56
0.0500	5.50	6.50
0.0500	7.50	6.00

Table 2—Effect of Varying $[H^+]$, μ and $[Mn^{2+}]$ on the Rate Constants

$[Amine] = 0.05\ mol\ dm^{-3}$; $[Mn(III)] = 3.77 \times 10^{-3}\ mol\ dm^{-3}$; temp. $= 35°C$

$[H^+]$ (mol dm^{-3})	$[Mn^{2+}]$ (mol dm^{-3})	μ (mol dm^{-3})	$k_{obs} \times 10^2$ (min^{-1})
0.50	0.02	2.00	13.82
0.60	0.02	2.00	11.52
0.75	0.02	2.00	9.98
0.85	0.02	2.00	8.25
1.00	0.02	2.00	6.50
1.25	0.02	2.00	6.00
1.00	0.02	2.15	6.90
1.00	0.02	2.25	7.10
1.00	0.02	2.30	7.60
1.00	0.02	2.40	8.10
1.00	0.025	2.00	6.70
1.00	0.030	2.00	6.70
1.00	0.04	2.00	6.80
1.00	0.05	2.00	6.70

Scheme 1

monoprotonated amine present in small amount due to the equilibrium

$$[Amine\ H^+]_{di} \rightleftharpoons [Amine\ H^+]_m + H^+$$

Since k_{obs} is independent of either $[Mn(II)]$ or $[Mn(III)]$, the possibility of Mn(IV) as the active oxidant species is ruled out. The reactive oxidant species may be hydrated Mn(III). If the undecomposed manganese(III) acetate were the active species, this would lead to complex kinetics, since the reduction potentials of such complex Mn(III) acetate species would be much less than aquomanganese(III) and it would be expected that Mn(II) acetate would be readily oxidised to Mn(III) acetate by some radicals that would not oxidise Mn(II)$_{aq}$ to Mn(III)$_{aq}$, as observed in the oxidation of nitrite ion[5] and hydrogen peroxide[6].

Based on the results described above and considering the experimental conditions employed, the most probable mechanism may be given either by Scheme 1 or Scheme 2.

The presence of radicals (I), (II) and (III) in the oxidation of p-phenylenediamine to p-benzoquinone in water or in 50% v/v aq. methanol, was es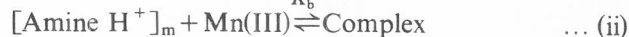tablished earlier by ESR studies[7-9]. Disproportionation of radical (I) to give radical (II) and parent amine ($2I \overset{K}{\rightleftharpoons} II$ + amine) can be neglected since the equilibrium constant, K is very small[9] ($3.5 \times 10^{-5}\ mol^2 dm^{-6}$). Under this condition the rate equation can be expressed by Eq. (1)

$$-\frac{\frac{1}{2}d\,[Mn(III)]}{dt} = k[complex]$$

$$= \frac{k_1 K[amine\ H^+]_{di}\,[Mn(III)]_T}{[H^+] + K[amine\ H^+]_{di}} \qquad \ldots (1)$$
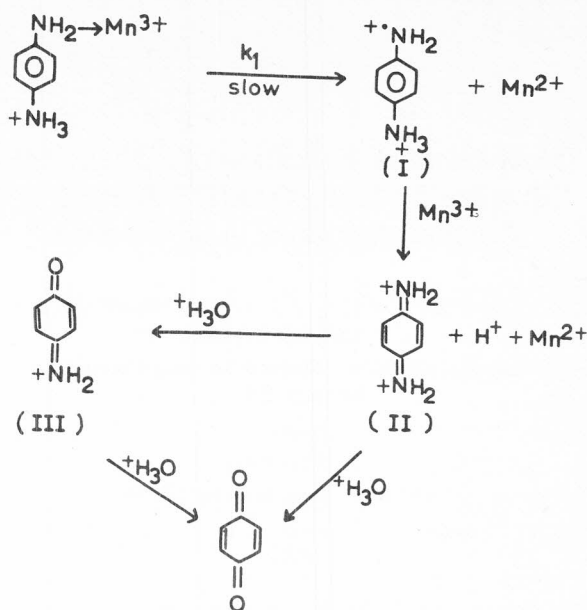
The pseudo-first order rate constant, k_{obs} is then given by Eq. (2)

$$k_{obs} = \frac{k_1 K[amine\ H^+]_{di}}{[H^+] + K[amine\ H^+]_{di}} \qquad \ldots (2)$$

$$[Amine\ H^+]_{di} \overset{K_a}{\rightleftharpoons} [Amine\ H^+]_m + H^+ \qquad \ldots (i)$$

$$[Amine\ H^+]_m + Mn(III) \overset{K_b}{\rightleftharpoons} Complex \qquad \ldots (ii)$$

$$Complex \overset{k_1}{\to} I + Mn^{2+} \qquad \ldots (iii)$$

$$I + Mn^{3+} \to II + Mn^{2+} \qquad \ldots (iv)$$

$$II \overset{hydrolysis}{\longrightarrow} III \overset{hydrolysis}{\longrightarrow} Product \qquad \ldots (V)$$

Scheme 2

In Scheme 2 involving monoprotonated amine, I, II and III represent the intermediates shown in reaction Scheme 1. Scheme 2 gives the observed rate as

$$-\frac{\frac{1}{2}d[Mn(III)]}{dt}$$

$$= \frac{k_1 K_a K_b[amine\ H^+]_{di}\,[Mn(III)]_T}{K_a K_b[amine\ H^+]_{di} + [H^+](1 + K_b[Mn(III)]_T)} \ldots (3)$$

Assuming $K_b[Mn(III)] \ll 1$, the pseudo-first order rate constant, k_{obs} is derived (Eq. 4) similar to Eq. (2)

$$k_{obs} = \frac{k_1 K_a K_b[amine\ H^+]_{di}}{[H^+] + K_a K_b[amine\ H^+]_{di}} \qquad \ldots (4)$$
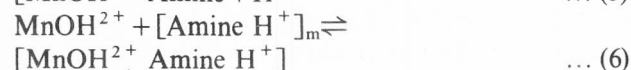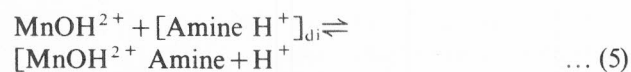
Although it is difficult to differentiate between the two mechanisms (Scheme 1 or Scheme 2) on kinetic data, on electrostatic reasons we believe that the Mn(III) ion reacts with small amount of monoprotonated form of p-phenylenediamine (Scheme 2) present in solutions rather than the diprotonated as assumed in the first mechanism (Scheme 1). Under the condition $[H^+] \ll [amine]$, all p-phenylenediamine will exist in the protonated form. We can, then, safely assume that

[amine H^+]$_{di}$ = [amine]$_T$. Equation (4) explains the observed kinetics. The values of K_aK_b and k_1 are obtained from (i) substrate variation ($K_aK_b = 1.6$ and $k_1 = 106 \times 10^{-2}$min^{-1}) and (ii) acid variation ($K_aK_b = 1.4$ and $k_1 = 90.9 \times 10^{-2}$min^{-1}).

The acid dependence can also be explained by the reaction[10]

$$Mn(III)_{aq} \underset{}{\overset{K}{\rightleftharpoons}} MnOH^{2+} + H^+$$

A combined role of Mn^{3+} and $MnOH^{2+}$ was proposed in most of the reactions involving Mn(III) in acid media and in fact $MnOH^{2+}$ was found to be more reactive than Mn(III)[11]. However this will not explain the dependence of k_{obs} on [substrate]. If we assume equilibria of the types (5) and (6)

$$MnOH^{2+} + [Amine\ H^+]_{di} \rightleftharpoons$$
$$[MnOH^{2+}\ Amine + H^+] \qquad \ldots (5)$$
$$MnOH^{2+} + [Amine\ H^+]_m \rightleftharpoons$$
$$[MnOH^{2+}\ Amine\ H^+] \qquad \ldots (6)$$

then the $1/k_{obs}$ should depend on $[H^+]^2$. This should also be valid for the interaction of unprotonated amine with Mn(III)$_{aq}$. However, experimental results are contrary to this.

The reaction has been studied at four different temperatures from which the activation parameters for overall reaction are calculated. The values found for $\Delta H^\ddagger = 46.25$ kJ mol^{-1} and $-\Delta S^\ddagger = 119.3$ J K^{-1} mol^{-1}.

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